

DEHYDROXYLATION REACTION KINETICS OF SOME INDIAN KAOLINITIC CLAYS

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ABSTRACT. The kinetic parameters for the dehydroxylation process of five Indian kaolinitic clays have been found out experimentally. The results obtained by thermogravimetric and differential thermal analysis methods showed fair agreement. The dehydroxylation reaction for all the clays obeyed first order kinetics. Activation energy for Bhandak clay was found to be highest indicating it to be most well crystallised kaolinite.

INTRODUCTION

When a kaolinitic clay is heated there is loss of structural hydroxyls between about 500-700°C. This process is known as dehydroxylation, since during this operation the neighbouring (OH) radicals in the kaolinite structure coalesce together to form water vapour.

A prior knowledge about the dehydroxylation characteristics of a clay is of much advantage to the ceramic industry where during manufacture, the body is almost invariably heated beyond this temperature range, and the strength which is rendered to the ware, before and after firing, is one of the principal considerations in selecting a clay for a particular purpose.

Work on the dehydroxylation reaction kinetics of a large number of clays has been reported previously by several authors (Murray and White, 1949, 1955; Vaughan, 1955, 1958; Brindley and Nakahira, 1957). No work in this direction on Indian clays has come to the notice of the authors.

In the present communication results on the dehydroxylation kinetics of a few Indian kaolinitic clays are presented, obtained by using thermogravimetric and differential thermal analysis methods and the activation energy and frequency factors for the reaction calculated.

THEORETICAL CONSIDERATIONS

Thermogravimetric method

Weight loss measurements as a function of time at different temperatures in the dehydroxylation peak region were used for determining kinetic parameters by the thermogravimetric method.

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Let w be the amount of clay present at any instant t and K_T the corresponding rate constant at temperature T . Assuming that the dehydroxylation process obeyed first order kinetics, and employing the general principle laid by Guggenheim (1926), it follows that

$$\frac{dw}{dt} = -K_T w \quad \dots (1)$$

$$\text{or} \quad w = w_0 e^{-K_T t} \quad \dots (2)$$

where w_0 is the amount of the reacting material present at time $t = 0$. If ΔL represents loss in weight of the clay during the time interval Δt , then at time $(t + \Delta t)$ we have

$$w - \Delta L = w_0 e^{-K_T(t + \Delta t)} \quad \dots (3)$$

Combining (2) and (3)

$$\log_{10} \Delta L = -(0.4343 K_T) t + \log_{10} w_0 (1 - e^{-K_T \Delta t}) \quad \dots (4)$$

Hence if $\log_{10} \Delta L$ vs t plot for a certain constant time interval Δt , at any experimental temperature T , gives a straight line a first order kinetics is indicated and from the slope K_T can be evaluated. Equation (4) thus enables the rate constants at different temperatures to be evaluated graphically.

$$\text{From Arrhenius equation} \quad K_T = A e^{-E/RT} \quad \dots (5)$$

$$\text{or} \quad \log_{10} K_T = \frac{(0.4343 E)}{R} \left(\frac{1}{T} \right) + \log_{10} A \quad \dots (6)$$

where E is the activation energy and $\log_{10} A$ the frequency factor. Equation (6) indicates that the plot of $\log_{10} K_T$ vs $1/T$ should be a straight line, and from the attributes of the same E and $\log_{10} A$ can be evaluated.

Differential thermal analysis method

The variation in dehydroxylation peak temperature with different heating rates was used for determining the kinetic parameters by differential thermal analysis method.

Combining equations (1) and (5) above dealt already under thermogravimetric method

$$\frac{dw}{dt} = -A w e^{-E/RT} \quad \dots (7)$$

$$\text{or} \quad \frac{d^2 w}{dt^2} = -A e^{-E/RT} \frac{dw}{dt} + \frac{E}{RT^2} \frac{dw}{dt} \frac{dT}{dt} \quad \dots (8)$$

At peak maximum (T_m) in the differential thermal analysis curve $\frac{d^2 w}{dt^2} = 0$

Hence
$$\ln \frac{\beta}{T_m^2} = \frac{(-E)}{R} \cdot \frac{1}{T_m} + \ln \frac{AR}{E} \quad \dots (9)$$

where $\beta = dT/dt$ (heating rate).

Thus if the dehydroxylation process obeyed first order kinetics $\ln \frac{\beta}{T_m^2}$ vs $\frac{1}{T_m}$ plot should be a straight line, from which E and frequency factor $\log_{10} A$ can be evaluated.

EXPERIMENTAL

Thermogravimetric analysis

The thermogravimetric analysis was done with the apparatus described by Sen (1958). The buoyancy correction for the heating cycle of thermobalance was determined by using calcined alumina as the reference material. The samples were first preheated at 410°C to constant weight, transferred in a platinum boat, keeping the same exposed area through all experiments, and readings of the weight loss taken as a function of time at different temperatures in the dehydroxylation peak region.

Differential thermal analysis

For D.T.A. curves, the apparatus described by Atma Ram *et al.*, (1955) was used, which enabled any heating rate between 1–15°C/min, to be adjusted within an accuracy of $\pm 0.1^\circ\text{C}$. Before taking D.T.A. run, the samples were agated to pass through 200 mesh Tyler, and stand in vacuum for at least four days over a saturated solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Calcined alumina of equal fineness was used as the reference inert material. The temperature thermocouple was located in the inert material and peak temperatures obtained reported as such.

RESULTS

Isothermal dehydration curves of Beldanga clay at 6 different temperatures in the dehydroxylation peak region are given in Fig. 1. $\log_{10} \Delta L$ vs t plots for this clay are given in Fig. 2.

D.T.A. curves at different heating rates of the clays are given in Fig. 3. Utilizing equations (6) and (9), Fig. 4 shows the Arrhenius plots for the different clays. The calculated values of the activation energy and frequency factor for the dehydroxylation process of the different clays are given in Table I.

DISCUSSION

Fig. 4 shows that $\log_e \frac{\beta}{T_m^2}$ vs $\frac{1}{T_m}$ plots for all the clays under study are linear indicating that their dehydroxylations obey first order kinetics.

Amongst all the kaolins under study, that from Bhandak region showed the highest activation energy (42.36 K Cal/mol/ $^\circ\text{K}$)(Table I). This indicates a stronger

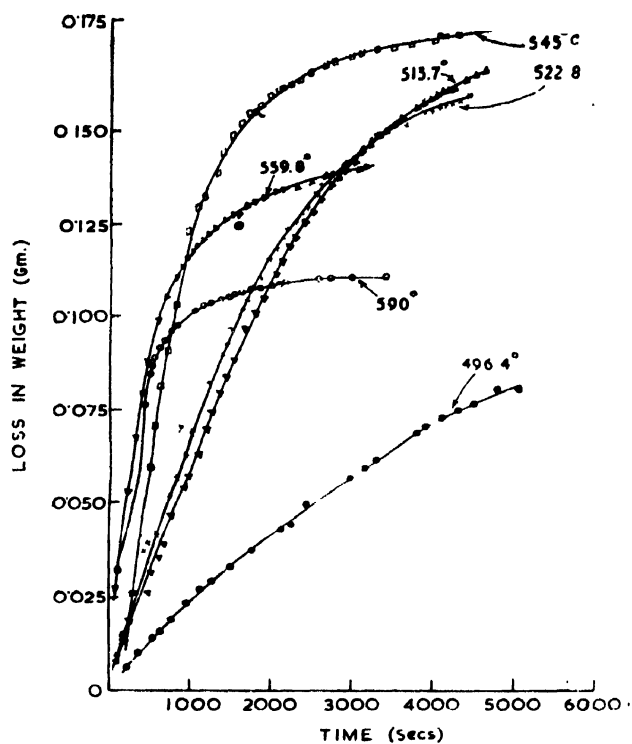


Fig. 1. Isothermal dehydration curves of Beldanga clay at different temperatures.

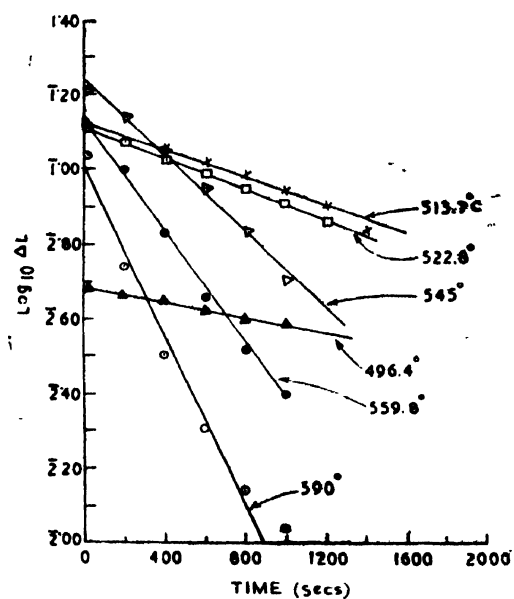


Fig. 2. $\text{Log}_{10} \Delta L$ vs t plots of Beldanga clay at different temperatures
(Derived from Fig. 1 taking $\Delta t = 2400$ secs.)

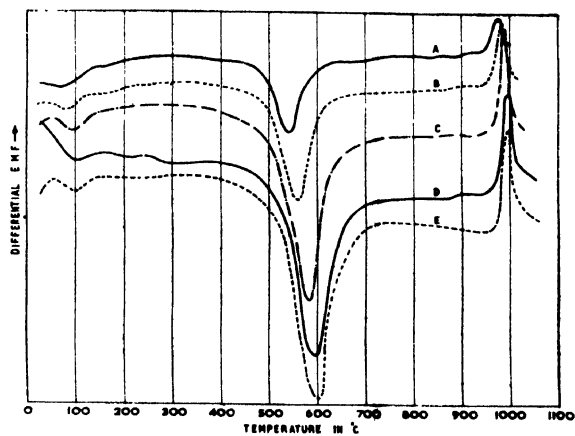


Fig. 3. (1) A, B, C, D, E Curves at 3, 6, 9, 12 and 15°C/min. respectively.

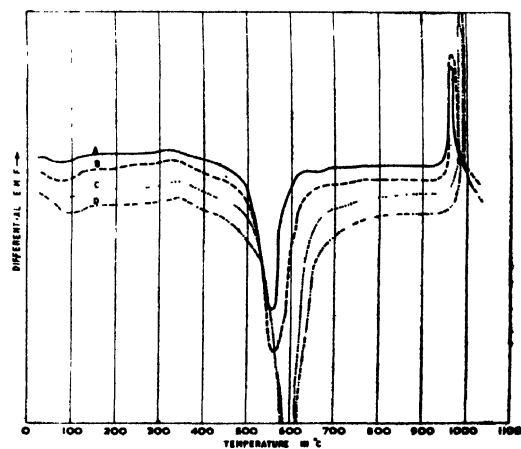


Fig. 3. (2) A, B, C, D—curves at 6, 9, 12 and 14.6°C/min. respectively.

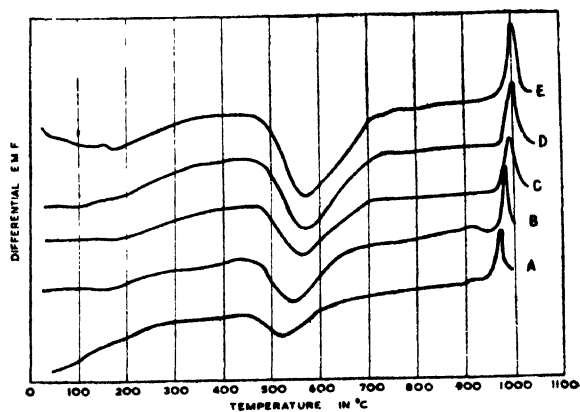


Fig. 3. (3) A, B, C, D, E—curves at 3, 6, 9, 12 and 14.9°C/min. respectively.

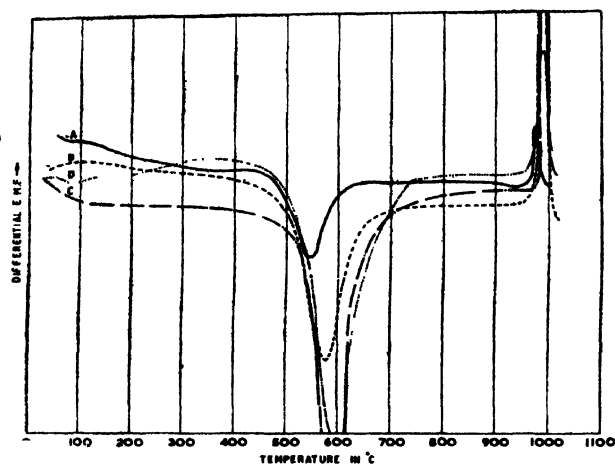


Fig. 3. (4) A, B, C, D —curves at 6, 9, 12 and 14.6°C/min. respectively.

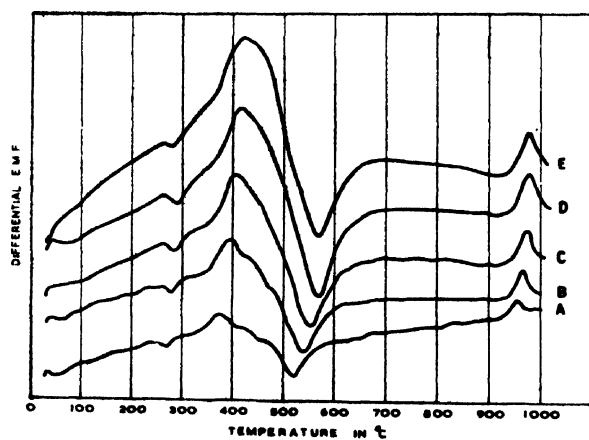


Fig. 3. (5) A, B, C, D, E —curves at 3, 6, 9, 12 and 14.9°C/min. respectively.

TABLE I

Activation energy and frequency factor for the dehydroxylation process for some Indian clays

Clay	Activation energy, E (K cal/mol/°K)	Frequency factor, $\log_{10} A$
Kusumpur	37.18	9.00
Kot Ransipur	30.53	7.03
Bhandak	42.36	10.60
Rajmahal	39.74	9.57
Beldanga	38.79	9.66

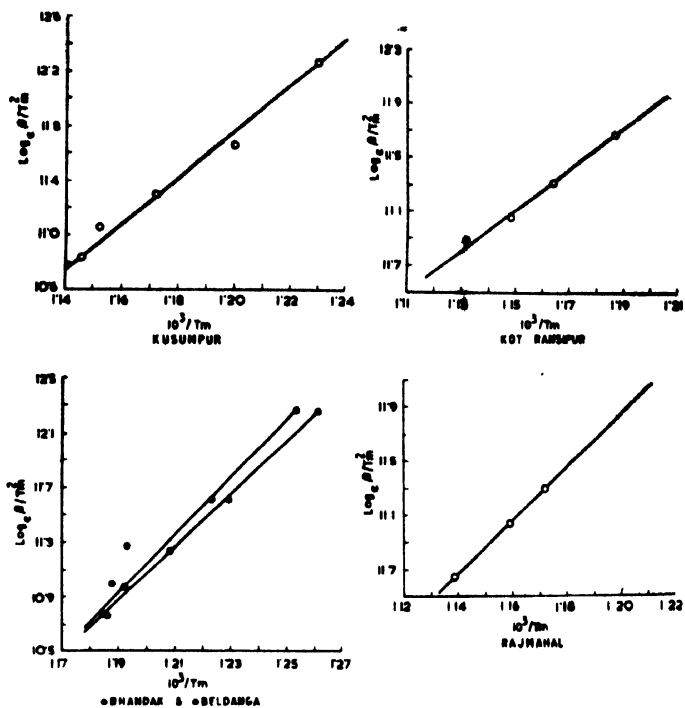


Fig. 4 Arrehenius plots of some Indian clays.
(A) D.T.A. method,

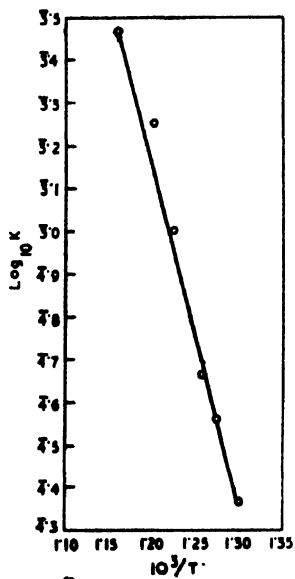


Fig. 4. (B) Thermogravimetric meth

bonding and more ordered structure in it, which evidence is also corroborated from X-ray analysis and electron microscopy results (Bishui and Prasad, 1959; Prasad, 1961).

A comparison of the results obtained for E and $\log_{10}A$ of Beldanga clay by thermogravimetric and differential thermal analysis methods (Fig. 4) showed fair agreement between them. This suggests that for evaluating kinetic parameters of kaolinitic clays, less time consuming D.T.A. method may be preferred in place of thermogravimetric method wherein considerable computation work is involved.

The dehydroxylation of kaolinite is not instantaneous but spreads over a fairly large temperature interval. This indicates that possibly the frequency factor in the dehydroxylation of kaolinite is related to the probability with which the (OH) radicals in the kaolinite structure combine when a certain threshold energy has been given to the system.

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